

SYNERGISTIC EFFECTS OF HYBRID HYDROGEN DONORS TOWARDS STABILIZATION OF PARAFFINIC JET FUELS IN THE PYROLYTIC REGIME

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ABSTRACT

The chemical interactions between n-tetradecane and the hybrid hydrogen donors of benzyl alcohol and 1,2,3,4-tetrahydro-1-naphthol, and benzyl alcohol and tetrahydronaphthalene have been studied. Compared to the use of a single hydrogen donor, the hybrids resulted in synergistic effects towards reducing the pyrolytic degradation of alkanes in jet fuels, resulting in an enhanced suppression of the formation of free radicals.

INTRODUCTION

Future high performance jet fuels are expected to be thermally stable at temperatures up to 900°F¹. Commercially available aviation fuels are high in paraffins, resulting in poor thermal performance due to their tendency to crack under these pyrolytic conditions². Hydrogen donors have been found to stabilize the fuels by terminating the propagation of free radicals from the cracking process^{3, 4}. The pyrolytic cracking of paraffins generates both primary and secondary free radicals, where a certain hydrogen donor may favor the interaction with only one type of free radical. This has been indicated previously, where the effects of hydrogen donors, such as benzyl alcohol (BA) and 1,2,3,4-tetrahydro-1-naphthol (THNol), on the product distribution of pyrolytic stressed tetradecane were studied⁵. Benzyl alcohol was found to reduce the amount of n-alkane cracking products, while THNol greatly reduced the 1-alkene. This was associated with the ability of BA to target primary radicals and, correspondingly, the targeting of THNol towards secondary radicals. Accordingly, this paper focuses on the potential of hybrid hydrogen donor for enhanced pyrolytic stabilization of paraffinic compounds typical for jet fuels. Hybrids of benzyl alcohol with tetrahydronaphthalene and 1,2,3,4-tetrahydronaphth-1-ol have been studied, and their synergistic effect upon tetradecane has been characterized.

EXPERIMENTAL

The compounds used were n-tetradecane (TD, Aldrich 99%), benzyl alcohol (BA, Aldrich 99.8%) tetrahydronaphthalene (THN, Aldrich 99%) and 1,2,3,4-tetrahydro-1-naphthol (THNol, Acros 97%). Stressing of TD alone or in different mixtures with one or two hydrogen donors, were performed for 30 minutes in a fluidized sandbath at 425, 450 and 475°C. A detailed description of the experimental setup and analytical determination of the product distribution using GC and GC/MS, has been reported elsewhere^{2, 5}.

RESULTS AND DISCUSSION

The thermal stability of tetradecane, TD, during the pyrolytic stressing can be expressed on the basis of the amount of TD remaining in the liquid over the amount in the original mixture weighed against the liquid yield of the experiment. This ratio is therefore normalized, and its enhancement when a hydrogen donor is added, compared to that of the TD alone, indicates that the hydrogen donor is indeed improving the thermal stability of the paraffinic compound. Figure 1 shows the remaining TD content over its initial concentration, stressed alone at 425, 450 and 475°C and its mixture with 0.5, 1, 3 and 5 mole% tetrahydronaphthalene (THN). With increasing stressing temperature, there is a dramatic decrease in the TD remaining content with no THN added, from around 85 mole% at 425°C to 27 mole% at 475°C. When THN is added at 425°C, there is a dramatic increase for the first mole% of hydrogen donor added up to 98% and it

stays stable at this level with further increase in the THN content. As the temperature is increased to 450°C, the TD remaining ratio for the TD stressed alone has been reduced to 56%. Again, there is a sharp increase up to 70% after only 0.5 mole% THN, and with further rise in the THN content, this ratio is slowly but steadily increasing to above 80% with 5 mole% THN addition. Increasing the temperature to 475°C, there is again a significant increase for the first half mole% THN added, as for the previous temperatures. A slower but steady rise is observed thereafter up to 5 mole% THN, reaching a TD remaining ratio of close to 50%. Similar behavior for the single addition of BA and THNol with TD has also been found⁵.

The GC traces of the liquid product distribution for TD alone and its mixture with 0.5 mole% THN, stressed at 475°C for 30 minutes, are plotted in Figure 2. As expected, the TD peak is the dominant peak, accounting for a major part of the total peak area. When no THN was added, as is the case for the top trace, a significant part of the total peak area is taken by the products from the thermal cracking of TD. To the left of the TD peak there are typical traces of linear alkanes and alkenes cracking products in the range of C4 to C13. The alkane and alkene with the same carbon number appear in pair, where the alkane is eluted at slightly lower retention times than the alkene, i.e. to the left. When the THN is added, the cracking products are greatly reduced as shown by the reduction in the peak heights and areas of the alkane and alkene derivatives in the bottom trace of Figure 2. The decrease in cracking products obtained by the addition of THN is therefore closely related to the reduced cracking of the TD. Further, the introduction of THN seems to especially reduce the 1-alkene peak in relation to the corresponding alkane peak, when compared to the TD stressed alone. Therefore, the THN seems to particular target the secondary radicals, similar to that found for THNol⁵. Figure 3 shows the ratio of the 1-alkene peak area over that of the corresponding n-alkane for TD alone and with 0.5 mole% THN and BA addition. There is a clear increase in the alkene/alkane ratio for the BA mixture, indicating that BA is indeed targeting the primary radicals. However, for the THN the ratios of the alkene over the alkane peaks are smaller than those observed for the TD alone, indicating that THN targets secondary radicals.

The observed effects on the thermal stabilization of TD by BA, THN and THNol are summarized in Scheme 1. The increased thermal stability of TD when hydrogen donors are added can be linked to the ability of the hydrogen donor to capture radicals formed during the stressing and therefore hinder the cracking. This results in an increased liquid product and enhances the TD remaining ratio, when compared to TD stressed alone. Scheme 1 presents in a simplified manner the role of the different hydrogen donors in the thermal stabilization of TD. A hydrogen is abstracted from the n-tetradecane due to the influence of heat into a secondary radical. The additive can then cap the radical at this stage, preventing the propagation of the reaction and leave the TD intact. THN and THNol have shown good ability to operate on secondary radicals as discussed above. However, if this radical is not stopped, it will undergo a β -scission, yielding a 1-alkene and a primary radical. These primary radicals are targeted by BA⁵. Accordingly, hybrids of BA and THN or BA and THNol should therefore produce synergetic effects at low concentrations towards enhanced thermal stabilization of TD.

Figure 4 compares the TD remaining ratio at 450°C for the TD mixed with a single hydrogen donor, BA, THN or THNol at 1 mole% addition, and that of TD added a hybrid of BA and THN or BA and THNol, at 0.5 mole% each. When added alone, both THN and THNol gave higher thermal stability than that of BA. However, the hybrid of 0.5 mole% BA and 0.5 mole% THN resulted in a clear enhanced thermal stability effect when compared to the 1 mole% single mixtures. This trend is further supported by the studies at 475°C, as shown in Figure 5. For the single hydrogen donor additions at 475°C, the TD remaining ratio increases from 27% for TD alone to around 35% after 1 mole% BA addition, and the use of THN has an even higher impact, where this ratio is around 46% (Figure 5). The hybrid of BA and THN would be expected to be in the range of 35 to 46%, but gave a result of 52% showing a clear synergistic effect between these two hydrogen donors. Correspondingly, the effect from the hybrid of BA and THNol would be expected to be in the range 35 to 39%, but showed an enhancement up to

46%. Although the BA/THN hybrid showed overall higher thermal stability effect at both 450 and 475°C, the synergistic effect from the BA/THNol hybrid was larger when taking into account the effect of the single hydrogen donors. These results are very promising for the development of additives that can work in both the autoxidative regime (150-250°C) and the pyrolytic regime, and further research will study the effect in both these regimes.

CONCLUSIONS

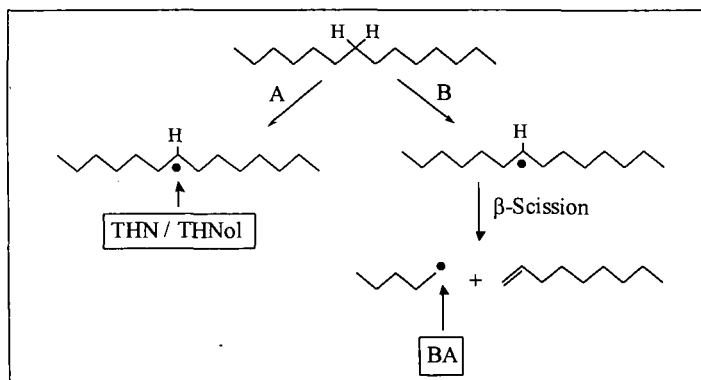
Hybrid hydrogen donors of (i) benzyl alcohol (BA) and tetrahydronaphthalene (THN), and (ii) benzyl alcohol (BA) and 1,2,3,4-tetrahydro-1-naphthol (THNol), have shown a synergistic effect on the thermal stabilization of tetradecane (TD) in the pyrolytic regime. The BA/THN hybrid showed the overall highest ability to stop the thermal decomposition of the paraffinic TD, but the BA/THNol hybrid showed the highest synergistic effect when compared to the BA and THNol alone.

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Scheme 1. Simplified role of the hydrogen donors, BA, THN and THNol on the thermal stabilization of TD in the pyrolytic regime.

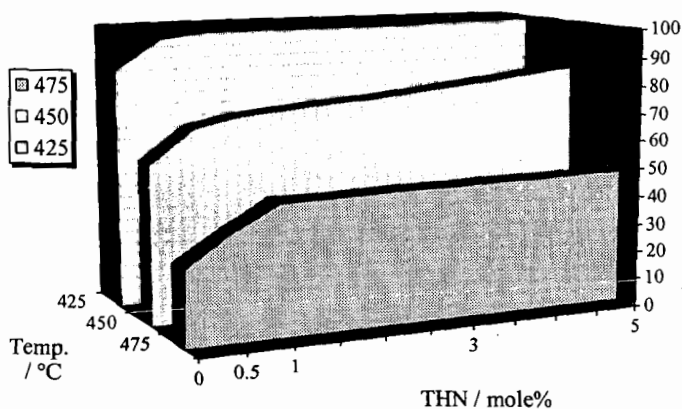


Figure 1. Comparison of remaining TD content over its initial concentration for different mixtures with tetrahydronaphthalene (THN) stressed at 425, 450 and 475°C for 30 minutes.

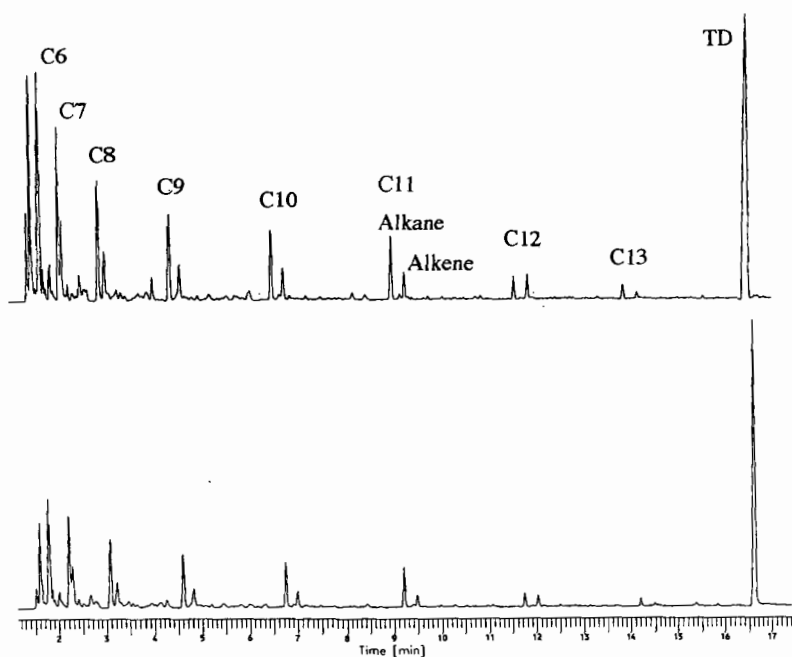


Figure 2. The GC traces of the liquid product distribution for TD alone (top) and its mixture with 0.5 mole% THN (bottom) stressed at 475°C for 30 minutes.

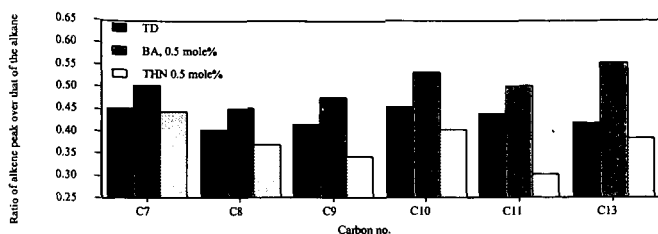


Figure 3. Ratio of the 1-alkene peak area over that of the corresponding alkane for TD alone and with 0.5 mole% THN and 0.5 mole% BA addition stressed at 475°C for 30 minutes.

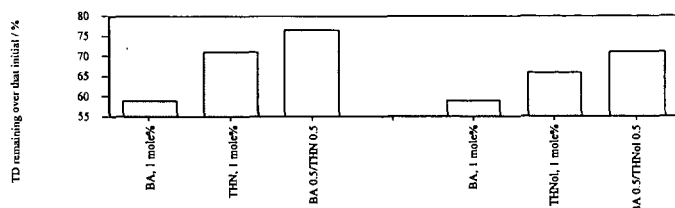


Figure 4. Comparison of the ratio of TD remaining over that initial for TD mixed with 1 mole% of the single hydrogen donors BA, THN and THNol, individually, and the effect of hybrids at 450°C.

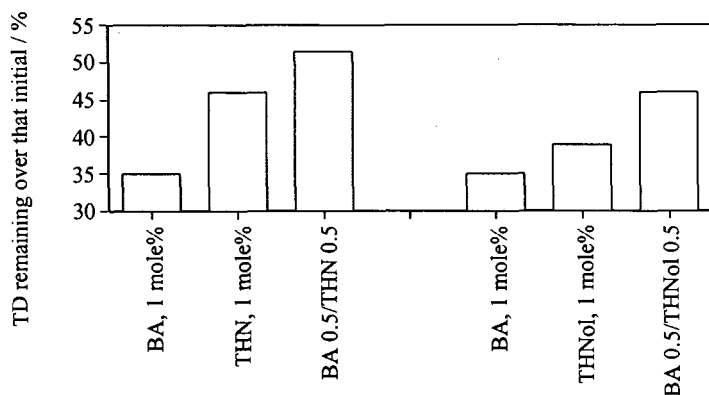


Figure 5. Comparison of the ratio of TD remaining over that initial for TD mixed with 1 mole% of the single hydrogen donors BA, THN and THNol, individually, and the effect of hybrids at 475°C.